A Different Approach to Detection Limits

Rock J. Vitale, CEAC; Erin E. Rodgers; Ruth L. Forman, CEAC - Environmental Standards, Inc., Valley Forge, PA
William J. Rogers, Neil E. Carriker - Tennessee Valley Authority, Harriman, TN

Abstract

State Agencies often require data to be reported to the method detection limit (MDL) for various programs, typically for the purpose of meeting health-based standards or for demonstrating compliance with a discharge permit. Commercial environmental laboratories typically perform MDL studies in accordance with 40 CFR part 136, Appendix B to determine matrix-specific and analyte-specific MDLs for a given preparative technique and analytical method. This method of determination of the MDL has endured significant technical criticism, but remains the most wide-spread method for determining the MDL. Unfortunately, calculating the MDL at the 99% confidence interval allows for the probability that 1% of the samples analyzed with a true concentration at the MDL will be reported as false negatives. Additionally, reporting data to the MDL does not control the possibility for false positives given the propensity for a Gaussian distribution of environmental sample results about the mean. In order to generate detection limits with a high degree of defensibility and show that a particular analyte can be "seen" at the MDL, project-specific MDLs for metals analyzed by ICP and ICP/MS in aqueous, solid, and biological matrices were developed for a large multi-year environmental clean-up utilizing months of blank data. Additionally, with each analytical sequence over years of metals analyses, a series of MDL standards were required to be analyzed to demonstrate the laboratory's ability to detect the project-specific MDL. This poster will discuss the development of the project-specific MDLs and the results from implementation of these MDLs with several years' worth of data for the MDL standards.

Background

- Regulators who are charged with being protective of human health and the environment often require project investigatory data to be reported to the MDL, specifically for the purpose of meeting health-based standards or for demonstrating compliance with a discharge permit.
- Risk assessors often request analytical data to be reported as low as possible and with a high degree of confidence and defensibility.
- Commercial environmental laboratories often perform MDL studies in accordance with 40 CFR Part 136, Appendix B to determine matrix-specific and analyte-specific MDLs for a given preparative technique and analytical method.
- The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Limitations with 40 CFR Part 136 Appendix B MDL Studies

- Can be defined as the smallest analyte concentration that can be demonstrated to be different from zero.
- The absence of a result at or above this value is inconclusive, false negative rate at this value is 50%.
- This procedure does not account for bias that may be introduced in the measurement from the blank water used when calculating the 40 CFR MDL.
- Reporting data to the MDL does not control the possibility for false positives given the propensity for a Gaussian distribution of environmental sample results about the mean and the possibility of a non-zero blank signal.
- If a laboratory spikes at a low concentration, MDLs could be calculated that are not achievable.
- This method of determination of the MDL has endured significant technical criticism but remains the most wide-spread method for determining the MDL.

Approach – Project-Specific Detection Limits

- In order to generate detection limits with a high degree of defensibility that were low enough to meet risk-based limits and show that a particular analyte can be "seen" at the detection limit (DL), project-specific DLs for metals analyzed by ICP and ICP/MS in aqueous, solid, and biological matrices were developed for a large multi-year environmental cleanup utilizing months of blank data.
- With each analytical sequence, a series of DL spike standards were analyzed to demonstrate the laboratory's ability to detect the project-specific DL.
- Laboratories evaluated method blank data:
  - Determine mean of blank data and standard deviation of blank data.
  - The project-specific DL (pDL) equals the average blank concentration plus three times the standard deviation of the blanks.
  - pDL = avg + 3σ
- "40 CFR MDL" and "avg + 3σ" are compared and the pDL is set as the higher of the two values.
- Examples of setting pDL

	Analyte	40 CFR MDL (µg/L)	Average Blank	Blank STDEV	Avg Blank + (3 * STDEV) (µg/L)	1x pDL	2x pDL	3x pDL	pDL (µg/L)	RL (µg/L)
	Arsenic	0.017	0.0639	0.0667	0.264	0.33	0.5	1	0.33	2
Lab 1	Selenium	0.038	0.0612	0.0792	0.2988	0.33	0.5	1	0.33	2

- pDLs for As and Se were calculated as 0.26 µg/L and 0.29 µg/L, respectively. Both were higher than the 40 CFR MDLs but were sufficiently low to meet human health and ecological risk assessment needs. Laboratory set the pDL at 0.33 µg/L for ease in creating spike standards.

	Analyte	40 CFR MDL (µg/L)	Average Blank	Blank STDEV	Avg Blank + (3 * STDEV) (µg/L)	1x pDL	2x pDL	3x pDL	pDL (µg/L)	RL (µg/L)
	Arsenic	0.291	0.0063	0.0305	0.098	0.29	0.58	0.87	0.291	1
Lab 2	Selenium	0.702	0.0227	0.0676	0.225	0.7	1.4	2.1	0.702	2

- pDLs for As and Se were calculated at values less than the 40 CFR MDL; accordingly, the pDLs were set at the 40 CFR MDLs. The MDLs were verified with each analytical sequence.

Data Assessment and Evaluation

- Raw data for verification standards are included in data packages to allow for data validation.
- US EPA validation guidelines do not include assessment pertaining to MDL verification standards.
- Approach to evaluation:
  - Each verification standard evaluated until analyte detection is observed. An analyte is considered "detected" if it is observed above the laboratory's 40 CFR MDL.
  - Is the 1× pDL verification standard "seen" at or above the 40 CFR MDL?
    - Yes - all data are reported at the pDL.
    - No - the pDL for all "not-detected" results raised to the 2× pDL (if seen).
  - Is the 2× pDL verification standard "seen" above the 40 CFR MDL?
    - Yes - for analytes not detected above 40 CFR MDL in the 1× pDL standard, raise the pDL for not-detects to 2× pDL level.
    - No - the pDL for all not-detected results raised to the 3× pDL (if seen).
  - Is the 3× pDL verification standard "seen" above the 40 CFR MDL?
    - Yes - for analytes not detected above 40 CFR MDL in the 2× pDL standard, raise the pDL for not-detects to 3× pDL level.
    - No - the laboratory must perform corrective action and sample reanalysis required.

Examples

					1x pDL		2x pDL		3x pDL	
	Analyte	40 CFR MDL (µg/L)	Avg Blank + (3 * STDEV) (µg/L)	pDL (µg/L)	Spiked	Observed	Spiked	Observed	Spiked	Observed
	Arsenic	0.017	0.264	0.33	0.33	0.33	0.5	0.49	1	0.99
Lab 1	Selenium	0.038	0.2988	0.33	0.33	0.27	0.5	0.49	1	0.93

- As and Se were observed in the 1× DL standard at concentrations greater than the 40 CFR MDL; the laboratory confirmed detection of As and Se to the pDL value.
- For this sequence, data can be reported to the pDL with a high degree of confidence in the reported results.

					1x pDL		2x pDL		3x pDL	
	Analyte	40 CFR MDL (µg/L)	Avg Blank + (3 * STDEV) (µg/L)	pDL (µg/L)	Spiked	Observed	Spiked	Observed	Spiked	Observed
	Arsenic	0.291	0.098	0.291	0.29	0.30	0.58	0.57	0.87	0.80
Lab 2	Selenium	0.702	0.225	0.702	0.70	0.75	1.4	1.2	2.1	1.9

- As and Se were observed in the 1× DL standard at concentrations greater than the 40 CFR MDL; the laboratory confirmed detection of As and Se to the pDL value.
- For this sequence, data can be reported to the pDL with a high degree of confidence in the reported results.

					1x pDL		2x pDL		3x pDL	
	Analyte	40 CFR MDL (µg/L)	Avg Blank + (3 * STDEV) (µg/L)	pDL (µg/L)	Spiked	Observed	Spiked	Observed	Spiked	Observed
	Arsenic	0.017	0.264	0.33	0.33	0.015	0.5	0.46	1	0.98
Lab 1	Selenium	0.038	0.2988	0.33	0.33	0.35	0.5	0.51	1	1.2

- In the above example, arsenic was detected at a concentration < 40 CFR MDL in the 1× pDL verification standard; the DLs for any not-detected results for arsenic would be raised to the 2× pDL concentration.
- Arsenic was detected above the 40 CFR MDL in the 2× standard; data would be reported to the 2× pDL with a high degree of confidence.
- Selenium would be reported to the pDL with a high degree of confidence.

Summary of Data

- This method of determining the DL takes into account the background effects, analytical bias, and variance inherent in different analysts performing analysis.
- To evaluate the ability to detect the pDL, laboratories prepared a custom standard at the pDLs.
- 1×, 2×, and 3× pDL verification standards were prepared and analyzed with each analytical sequence.
- Because the pDL was set as the higher of the two values, analytes should not be detected in method blanks above the pDL.
  - Arsenic and selenium are the main constituents of concern for the project and the driver's for risk assessment.
  - Data were evaluated from September 2009 until September 2012; arsenic was detected above the pDL in only 5 method blanks during this timeframe.
  - Data were evaluated from September 2009 until September 2012; selenium was "not-detected" above the pDL in the method blanks during this timeframe.
- For all surface water data validated for the project, As and Se were reported to the DL for all samples.
- 1,500 1× pDL verification standards were evaluated for this paper.
  - Out of 1,500 1× DL verification standards:
    - Arsenic was detected < 40 CFR MDL in only two 1× pDL standards.
    - Selenium was detected < 40 CFR MDL in only 15 1× pDL standards.

Conclusions

- When MDL reporting is required, it is prudent to verify the reported MDL through the analysis of low-level standards to demonstrate that target analytes can truly be detected and reported down to the reported MDL.
- Evaluation of laboratory blank data, in conjunction with 40 CFR MDLs, is critical in establishing defensible project DLs, particularly for common laboratory contaminants.
- Verification of the pDL at the pDL requires custom standards, more QC in the analytical run, and additional evaluation of raw data.
- By evaluating blank data to determine pDLs and running verifications at 1×, 2×, and 3× of the pDL, data users can be more confident in the reporting of low-level results.
- The laboratory can set the As and Se pDL at a value low enough to meet risk-based standards, but a level high enough to be consistently detected.
- Data reported to this pDL level have a higher degree of confidence, which is a win-win for both the regulated party and the laboratory.

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